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THEORETICAL INVESTIGATIONS OF COLOR CENTERS IN ALKALI AZIDES.(U)  
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THEORETICAL INVESTIGATIONS OF  
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# TABLE OF CONTENTS

I. Publications and Theses	1
A. Publications	1
B. Papers presented at meetings	1
C. Theses	2
II. Investigations	3
A. Introduction	3
B. Properties of azides	3
C. Review of prior investigations	4
D. Polarized optical absorption and ESR of uv-irradiated $\text{NaN}_3$	4
E. Interstitial $\text{N}_2^-$ center in $\text{NaN}_3$	6
F. $\text{N}_4^-$ center in $\text{KN}_3$	7
G. $\text{N}_3^-$ ion	9
H. $\text{NH}_2$ in $\text{NaN}_3$	11
I. Discussion	12
III. References	15

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## I. PUBLICATIONS AND THESES

### A. Publications

1. R. H. Bartram and A. M. Stoneham,  
"On the luminescence and absence of luminescence  
of F centers", Solid St. Comm. 17, 1593-1598 (1975)
2. L. A. Kappers, P. K. Jain and R. H. Bartram,  
"Polarized optical absorption of uv-irradiated  
sodium azide", Phys. Rev. B14, 5473-5481 (1976)
3. R. H. Bartram, L. A. Kappers and G. G. DeLeo,  
"Electron-spin resonance of uv-irradiated sodium azide",  
Phys. Rev. B14, 5482-5489 (1976)
4. M. Stapelbroek, O. R. Gilliam and R. H. Bartram,  
"Transferred hyperfine interactions for trapped-hole  
centers in tetragonal  $\text{GeO}_2$ ", Phys. Rev. B2, 37-43 (1977)
5. R. H. Bartram and L. A. Kappers,  
"ESR identification of a new  $\text{N}_2^-$  defect in X-ray  
irradiated  $\text{NaN}_3$ ", J. Phys. Chem. Solids 38, 727-731 (1977)
6. A. R. Rossi and R. H. Bartram,  
"Low-lying excited states of  $\text{N}_3^-$ ",  
J. Chem. Phys. (in press)
7. P. J. Kemmey, R. H. Bartram, A. R. Rossi and P. W. Levy,  
"Fluorescence of potassium azide", J. Chem. Phys. (in press)
8. G. D. Bent, R. H. Bartram, A. R. Rossi and P. J. Kemmey,  
"Ab-initio calculations of the electronic properties of  
 $\text{N}_4^-$  in  $\text{KN}_3$ ", submitted to J. Phys. Chem. Solids.

### B. Papers presented at meetings

1. L. A. Kappers and R. H. Bartram,  
"Correlation of ESR and optical spectra of irradiated  
sodium azide", Bull. Am. Phys. Soc. 20, 807 (1975)
2. G. D. Bent, A. R. Rossi, R. H. Bartram and P. J. Kemmey,  
"Molecular orbital calculation of  $\text{N}_4^-$  in  $\text{KN}_3$ ",  
Bull. Am. Phys. Soc. 21, 436 (1976)
3. R. H. Bartram and L. A. Kappers,  
"ESR of a radiation-induced defect in  $\text{NaN}_3$ ",  
Bull. Am. Phys. Soc. 21, 780 (1976)

4. A. R. Rossi and R. H. Bartram,  
"Low-lying excited states of  $N_3^-$ ",  
Bull. Am. Phys. Soc. 22, 343 (1977)
5. D. A. Gordon and R. H. Bartram,  
"ESR of X-irradiated  $NaN_3$ ; evidence for  
trapped  $NH_2$  radicals",  
Bull. Am. Phys. Soc. 23, 397 (1978)

C. Theses

1. Gary D. Bent, "An ab initio calculation of the  
electronic properties of the  $N_4^-$  defect in  
potassium azide", Ph.D. thesis, University of  
Connecticut, 1977.

## II. INVESTIGATIONS

### A. Introduction

Alkali azides ( $\text{NaN}_3$ ,  $\text{KN}_3$ ,  $\text{RbN}_3$  and  $\text{CsN}_3$ ) are subject to coloration at low temperature by ionizing radiation,<sup>1-6</sup> and the resulting color centers have been invoked by a number of investigators in proposed mechanisms for thermal and photochemical decomposition.<sup>7-9</sup> The need for reliable identification and characterization of these defects has provided the motivation for our research, which involves theoretical investigations of specific defects, supplemented by correlated ESR and optical studies. Additionally, we have investigated low-lying excited states of the azide ion itself. It is anticipated that insights gained from this research will ultimately enhance our understanding of decomposition mechanisms not only in alkali azides, but also in lead azide, the most commonly used primary explosive. A significant spin-off of this research has been the improvement of computer software for quantum chemistry calculations at Picatinny Arsenal through the efforts of Captain Gary Bent.

### B. Properties of Azides

The structure and properties of azide compounds have been described in detail in a number of reviews.<sup>10-13</sup> The azide ion is a linear  $\text{N}_3^-$  molecule ion, which occurs as a unit in both organic and inorganic compounds. The azides are unstable against decomposition by the reaction  $2\text{N}_3^- \rightarrow 3\text{N}_2 + 2\text{e}^-$ , resulting in the evolution of nitrogen gas. The heavy metal azides (e.g.  $\text{PbN}_6$ ) are explosives with wide technological applications. Alkali azides are considerably more stable, but are subject to thermal<sup>8</sup> and photochemical<sup>7</sup> decomposition.

The structure of  $\text{NaN}_3$  is rhombohedral above room temperature and

monoclinic below, while  $\text{KN}_3$ ,  $\text{RbN}_3$  and  $\text{CsN}_3$  have a tetragonal structure. Consequently, in  $\text{NaN}_3$  all of the anion sites are identical, with the azide ions oriented parallel to one another (and to the hexagonal c-axis in the rhombohedral phase), whereas in  $\text{KN}_3$  there are two distinct transverse orientations of the azide ion which are mutually perpendicular.

Corresponding color-center absorption bands occur in  $\text{KN}_3$ ,  $\text{RbN}_3$  and  $\text{CsN}_3$ ,<sup>14,15</sup> whereas those in  $\text{NaN}_3$  are quite different.<sup>5,6</sup>

### C. Review of Prior Investigations

The color centers which have been previously identified in alkali azides by electron-spin resonance include F and  $\text{F}_2^+$  centers in  $\text{NaN}_3$ ,<sup>5,6,16</sup> substitutional  $\text{N}_2^-$  and interstitial  $\text{N}^\circ$  in  $\text{NaN}_3$  and  $\text{KN}_3$ ,<sup>17-22</sup> and  $\text{N}_4^-$  and  $\text{N}_3^{2-}$  in  $\text{KN}_3$ .<sup>22-25</sup> Point-ion and pseudopotential calculations for F and  $\text{F}_2^+$  centers in  $\text{NaN}_3$ ,<sup>26-28</sup> and a molecular-orbital calculation of ground-state properties of substitutional  $\text{N}_2^-$  in  $\text{NaN}_3$ ,<sup>29</sup> were performed under previous grants, DA-ARO-D-31-124-71-G35 and DAHCO4-74-G-0234. Experimental work performed under previous grants includes correlations of  $\text{N}_2^-$  and  $\text{N}_4^-$  ESR spectra in  $\text{KN}_3$  and  $\text{RbN}_3$  with optical absorption spectra,<sup>30,31</sup> and a systematic study of the growth and annealing of polarized optical absorption<sup>27</sup> and ESR<sup>32</sup> spectra in uv-irradiated  $\text{NaN}_3$ . The latter investigation was extended during the present grant period, and is reviewed in the following section.

### D. Polarized Optical Absorption and ESR Spectra of uv-Irradiated $\text{NaN}_3$

Optical absorption spectra were measured at 77 K for light polarized both parallel and perpendicular to the hexagonal c axis in relatively thick  $\text{NaN}_3$  single crystals, following uv-irradiation at 77 K and successive five-minute pulse anneals performed at 20 K intervals in the range 100 - 280 K.<sup>27</sup>

The resulting twenty-two spectra were decomposed into five distinct components with different temperature dependence and polarization. Bands at 610 nm in perpendicular polarization and 450 nm in parallel polarization were found to increase together by 25% near 140 K and to anneal together near 260 K; these bands correspond well in energy and polarization to  $A^+ \rightarrow A^-$  and  $A^+ \rightarrow B^-$  transitions of the  $F_2^+$  center, predicted by a point-ion calculation<sup>27</sup> to occur at 560 nm and 410 nm, respectively. Bands at 735 nm and 640 nm in perpendicular polarization, which anneal together near 140 K (except for a persistent component), correlate with the 19-line F-center ESR signal,<sup>16</sup> and correspond to  $A^+ \rightarrow A^-$  and  $A^+ \rightarrow B^-$  transitions of the F center, predicted by a point-ion calculation<sup>26</sup> to occur at 680 nm and 630 nm, respectively. These identifications of the  $F_2^+$  and F centers corroborate the assignments of Miller and co-workers<sup>5,6</sup> for the 610- and 735-nm bands, and are further supported by the inter-convertability of these centers. However, Miller's correlation of the 610-nm band with a broad ESR line<sup>5</sup> was not confirmed, and the origin of that ESR line has not been positively established, although it appears to correlate with the persistent component of the F-center optical absorption. This persistent component is probably due to F centers perturbed by proximity to another defect, such as an anion vacancy in a second-neighbor position, which stabilizes them and reduces their symmetry sufficiently to obliterate the 19-line hyperfine structure of their ESR spectrum.

A new optical absorption band at 565 nm in parallel polarization, which resembles the 565-nm band in  $KN_3$ ,<sup>30</sup> does not correlate with either the F or  $F_2^+$  centers. The annealing of the 565-nm band near 220 K occurs in two stages, accompanied respectively by the growth and decay of a spin-1 ESR

signal, corresponding to an exchange-coupled pair of spin- $\frac{1}{2}$  defects in second-neighbor anion sites.<sup>32</sup> It was inferred from relative intensity measurements of the spin-1 ESR signal at 77 K and 4.2 K that there is an antiferromagnetic exchange interaction of  $10 \text{ cm}^{-1}$ . Both annealing stages of the 565-nm band follow first-order kinetics, with activation energies of 0.64 eV for the fast stage and 0.90 eV for the slow stage. The defects responsible for the 565-nm band and spin-1 ESR signal have thus far eluded positive identification. Substitutional  $\text{N}_2^-$  was eliminated as a possibility, and none of the other models considered (linear and cyclic  $\text{N}_3^0$ ,  $\text{N}_4^-$  and  $\text{N}_3^{2-}$ ) is entirely satisfactory.

#### E. Interstitial $\text{N}_2^-$ Center in $\text{NaN}_3$

A relatively weak ESR spectrum is observed in  $\text{NaN}_3$ , irradiated with either uv or X-rays at 77 K, which has an anisotropic g-value and exhibits a resolved 5-line hyperfine structure with components in the ratio 1:2:3:2:1. This 5-line spectrum, which was investigated in detail in X-ray irradiated  $\text{NaN}_3$ ,<sup>33</sup> corresponds to a single unpaired electron interacting symmetrically with two spin-one nuclei in three inequivalent sites. It is attributed to interstitial  $\text{N}_2^-$  on the basis of measured hyperfine splittings and g-values. The molecule ion is at a point of  $\text{C}_{2h}$  symmetry between two adjacent azide ions, with its axis tilted  $66.5^\circ$  from the hexagonal c axis. The observed crystal-field splitting (as reflected in the g-values) and tilt angle agree well with theoretical values derived from an earlier molecular orbital calculation<sup>29</sup> for  $\text{N}_2^-$  combined with the calculated point-ion potential at the interstitial site. The ESR spectrum of interstitial  $\text{N}_2^-$  is clearly distinguishable from that of substitutional  $\text{N}_2^-$ , investigated earlier by Gelerinter and Silsbee.<sup>17,18</sup>

The 5-line spectrum exhibits a curious temperature dependence. Most of its intensity decays near 140 K, following the same annealing behavior as the nitrogen atom in X-ray irradiated  $\text{NaN}_3$  and the 19-line F-center ESR signal in uv-irradiated  $\text{NaN}_3$ . However, a component of the 5-line spectrum persists to room temperature, and is actually enhanced (by a factor of two) in the temperature range near 220 K where the spin-1 spectrum appears in uv-irradiated  $\text{NaN}_3$ . In the latter respect, it resembles the persistent component of the 735-nm band in uv-irradiated  $\text{NaN}_3$ , which is probably due to perturbed F centers. An enhancement of the 610-nm band in uv-irradiated  $\text{NaN}_3$  which is also observed in this temperature range, and is much more pronounced in "old" crystals, has been attributed to thermal ionization of metallic sodium.<sup>6</sup> All three enhancements may be due to the release of electrons from shallow traps, which are subsequently trapped at interstitial  $\text{N}_2$  molecules as well as at single and double vacancies. This view is supported by the observation of a thermally-stimulated current peak at the same temperature;<sup>34</sup> its activation energy of 0.99 eV conforms with that of the slow annealing stage of the 565-nm band.

#### F. $\text{N}_4^-$ Center in $\text{KN}_3$

The  $\text{N}_4^-$  radical was identified in  $\text{KN}_3$  by electron spin resonance.<sup>23</sup> Only the  $\text{N}_2^-$  radical is observed after uv irradiation at 77 K, but on warming to room temperature  $\text{N}_2^-$  disappears and  $\text{N}_4^-$  appears. The  $\text{N}_4^-$  radical is also produced directly by uv irradiation at room temperature.

The  $\text{N}_2^-$  and  $\text{N}_4^-$  ESR spectra have been correlated with optical absorption bands in uv-irradiated  $\text{KN}_3$ . A prominent band at 565 nm, which is produced by uv-irradiation at 77 K, is replaced by bands at 580 nm and 780 nm, with the same integrated optical density, on warming to room

temperature. Annealing of the latter two bands above room temperature is precisely correlated with that of the  $N_4^-$  ESR signal, and follows first-order kinetics with activation energy 0.92 eV. Annealing of the 565-nm band below room temperature is evidently related to that of the  $N_2^-$  ESR signal; however, the former follows first-order kinetics with activation energy 0.70 eV, while the latter cannot be fit with kinetics of any order and exhibits a persistent component. It has since been established that the 565-nm band cannot be a transition of the  $N_2^-$  ion,<sup>32</sup> and its origin remains undetermined.

More recently, the energies of the ground state and low-lying excited states of the  $N_4^-$  radical in  $KN_3$  were calculated using ab initio techniques.<sup>35,36</sup> A rectangular equilibrium geometry with dimensions 2.76 x 2.47 a.u. was first determined by calculating  $N_4^-$  as a free radical. (The defect was originally identified as linear  $N_4^-$ ;<sup>23</sup> however a linear geometry is incompatible with equal hyperfine interactions at the four nuclei.) In the  $X^2\Gamma_4^+$  ground state the unpaired electron is in a  $\pi$  orbital which is consistent with the experimental hyperfine tensor only if one edge of the  $N_4^-$  radical is parallel to the tetragonal c axis of  $KN_3$ . The free radical geometry was used to calculate the  $X^2\Gamma_4^+$  state of  $N_4^-$  in a point-ion crystal field appropriate to the anion site of  $KN_3$ . The calculated hyperfine constants,  $a = 2.1$  G,  $B_{xx} = -3.4$  G,  $B_{yy} = 7.0$  G and  $B_{zz} = -3.6$  G, were in good agreement with experiment. Several excited states of  $N_4^-$  were also calculated, and when an estimate of correlation energy was included, the transition energy of the  $A^2\Gamma_3^- \leftarrow X^2\Gamma_4^-$  transition agreed well with the 780-nm absorption band. However, it was established that no other transition of  $N_4^-$  can correspond with the 580-nm band, which must therefore arise from another defect which anneals together with  $N_4^-$  by a common mechanism.

In summary, the 780-nm band in uv-irradiated  $\text{KN}_3$  has been established as a transition of  $\text{N}_4^-$ , but the defects responsible for the 565- and 580-nm bands, which may be related, remain to be identified. The same defect may be responsible for the 565-nm band in both  $\text{KN}_3$  and  $\text{NaN}_3$ ; in each case, the transition is polarized parallel to the axis of the azide ion.<sup>27,30</sup>

#### G. $\text{N}_3^-$ Ion

The alkali azides are found to have very similar optical absorption spectra, which have been variously attributed to excitons<sup>37</sup> and to internal transitions of the azide ion.<sup>38-40</sup> The lowest energy transition appears to coincide with excitation spectra for fluorescence<sup>37,41</sup> and photolysis<sup>6,24,30</sup> as well. Ab initio SCF molecular orbital calculations on low-lying states of  $\text{N}_3^-$  were performed in an effort to achieve a better understanding of these processes.<sup>42</sup>

Calculations on linear, symmetric  $\text{N}_3^-$  were performed with the Hunt-Hay-Goddard open-shell program.<sup>43,44</sup> Both a  $[3s,2p]$  basis contracted from a primitive  $(9s,5p)$  gaussian basis, and the same basis augmented by polarization functions  $[3s,2p] + d$ , were employed at a fixed internuclear separation  $r_{\text{N-N}} = 2.225$  a.u. in calculating vertical excitation energies for the following states: ...  $4\sigma_g^2 3\sigma_u^2 1\pi_g^4, {}^1\Sigma_g^+$ ; ...  $1\pi_g^3 2\pi_u^1, {}^1,3\Sigma_u^+, {}^1,3\Sigma_u^-$ , and  ${}^1,3\Delta_u$ ; ...  $3\sigma_u^1 \dots 2\pi_u^1, {}^1,3\Pi_g$ ; and ...  $4\sigma_g^1 \dots 2\pi_u^1, {}^1,3\Pi_u$ . These calculations yielded the best ground state energy yet reported for  $\text{N}_3^-$ , -163.2932 a.u., and provided qualitative support for the spectral assignments of McDonald et al.,<sup>40</sup> who interpret the spectra as internal transitions of the azide ion. However, it was evident that resonances of the free  $\text{N}_3^-$  ion are not in precise quantitative agreement with the bound excited states of  $\text{N}_3^-$  in a crystal lattice.

The smaller basis  $[3s,2p]$  was used in calculating energies of the  ${}^1\Sigma_g^+$

ground state and the  ${}^3\Sigma_u^+$ ,  ${}^1,3\Sigma_u^-$  and  ${}^1,3\Delta_u$  states of linear, symmetric  $N_3^-$  as a function of internuclear separation. The equilibrium internuclear separation<sup>45</sup> and symmetric-stretching frequency<sup>46</sup> for the ground state are well established experimentally, and the corresponding quantities were determined for the  ${}^1\Sigma_u^-$  excited state from the resolved vibrational structure of the lowest-energy absorption band in  $KN_3$ .<sup>37</sup> The calculated equilibrium internuclear separations (2.225 a.u. for  ${}^1\Sigma_g^+$  and 2.385 a.u. for  ${}^1\Sigma_u^-$ ) were in precise agreement with experiment, while the calculated vibration frequencies ( $1470\text{ cm}^{-1}$  for  ${}^1\Sigma_g^+$  and  $1220\text{ cm}^{-1}$  for  ${}^1\Sigma_u^-$ ) were somewhat higher than the experimental values ( $1344$  and  $1015\text{ cm}^{-1}$ , respectively).

The  $[3s,2p]$  basis was also used in the IBMOL program of Clementi and Mehl<sup>47</sup> to calculate energies of the  ${}^1A_1({}^1\Sigma_g^+)$  ground state and the following low-lying triplet states of bent  $N_3^-$ :  ${}^3B_2({}^3\Sigma_u^+)$ ,  ${}^3A_2({}^3\Delta_u)$ ,  ${}^3B_2({}^3\Delta_u)$  and  ${}^3A_2({}^3\Sigma_u^-)$ . These triplet states belong to four distinct configurations of bent  $N_3^-$  which correspond to a single configuration of linear  $N_3^-$ . The interaction of these configurations was inferred by matching solutions at  $\theta = 180^\circ$ , and was assumed to be independent of  $\theta$ .

The calculations on bent  $N_3^-$  provided the key to interpretation of the fluorescence spectrum of  $KN_3$ .<sup>41</sup> One component of this fluorescence spectrum comprises seven resolved vibrational lines separated by  $720\text{ cm}^{-1}$  with the 0-0 transition at  $22,620\text{ cm}^{-1}$  (2.8 eV). The vibrational structure is clearly associated with the bending mode, and the absence of stretching-mode vibrations implies a transition between excited states. Analysis of the relative intensities of vibrational components shows that the bending angle changes by  $\Delta\theta = 19^\circ$  in the transition. Comparison with calculated energies leads to the assignment  ${}^3A_2({}^3\Sigma_u^-) \rightarrow {}^3B_2({}^3\Sigma_u^+)$ , for which the pre-

dicted 0-0 transition energy is 2.7 eV, and the predicted change in bending angle is  $\Delta\theta = 30^\circ$ . A second broad, featureless component with a maximum at 2.2 eV cannot be identified with certainty.

The excitation spectrum for fluorescence appears to coincide with the lowest energy absorption band,  $^1\Sigma_u^- \leftarrow ^1\Sigma_g^+$ . Evidently, absorption is followed by intersystem crossing to the nearly degenerate  $^3\Sigma_u^-$  state, a process enhanced by the long radiative lifetime of the  $^1\Sigma_u^-$  state. The radiative transition  $^3A_2(^3\Sigma_u^-) \rightarrow ^3B_2(^3\Sigma_u^+)$  is dipole allowed in the bent radical. The final state  $^3B_2(^3\Sigma_u^+)$  is then metastable, since it is the lowest-energy state for its equilibrium bending angle,  $\theta = 134^\circ$ . The calculations on bent  $N_3^-$  were performed for an internuclear separation N-N = 2.225 a.u.; however, it is clear from our symmetric stretching calculations that this is not the equilibrium separation for the triplet excited states. A tentative reconstruction of adiabatic potential energy surfaces suggests that the  $^3B_2(^3\Sigma_u^+)$  metastable state lies 1.3 eV above the ground state, with an equilibrium conformation N-N = 2.365 a.u.,  $\theta = 134^\circ$ ; and that the activation energy for non-radiative de-excitation is 0.2 eV. With an assumed frequency factor of  $10^{13} \text{ sec}^{-1}$ , appropriate to molecular vibrations, the lifetime of this metastable state at 77 K is of the order of one second.

#### H. NH<sub>2</sub> in NaN<sub>3</sub>

When single crystals of NaN<sub>3</sub> grown from aqueous solution are X-ray irradiated at 77 K and annealed at 200°C, a complex ESR spectrum is observed with a nearly isotropic g-value of 2.0036 and a highly anisotropic hyperfine structure.<sup>48</sup> This resonance has been assigned to NH<sub>2</sub> radical in three orientations at azide ion sites. The unpaired electron is in a  $\pi$  orbital whose nodal plane contains the hexagonal c-axis as bisector of the H-N-H

angle. Values of the proton hyperfine constants are somewhat anomalous, and suggest that both bond angles and bond lengths are slightly distorted in the azide-ion site. Superhyperfine structure from surrounding  $\text{Na}^+$  ions is observed at low temperature, and there is evidence for rapid reorientation at higher temperatures. The  $\text{NH}_2$  radicals are stable up to  $240^\circ\text{C}$ . The observation of this defect provides evidence that solution-grown crystals contain a substantial concentration of hydrogen.

### I. Discussion

The researches on color centers in alkali azides performed under the present grant and its predecessors have yielded a number of new insights and discoveries. Point-ion calculations of wave functions and energy levels of F and  $\text{F}_2^+$  centers in  $\text{NaN}_3$ <sup>26,27</sup> have corroborated these defect models and have served to identify their radiative transitions, including newly discovered absorption bands in each case. Molecular-orbital calculations on substitutional  $\text{N}_2^-$  in  $\text{NaN}_3$ <sup>29</sup> accounted for its measured g values and hyperfine parameters, and explained its orientation in terms of a phase transition rather than a Jahn-Teller effect.<sup>17</sup> The 780-nm band in  $\text{KN}_3$  has been identified as a transition of  $\text{N}_4^-$  both by correlated optical and ESR annealing measurements<sup>30</sup> and by an ab-initio molecular orbital calculation.<sup>35,36</sup> Similar but less precise correlations have been established for  $\text{RbN}_3$  and  $\text{CsN}_3$ .<sup>31</sup>

Newly discovered defects include interstitial  $\text{N}_2^-$ <sup>33</sup> and substitutional  $\text{NH}_2$ <sup>48</sup> in  $\text{NaN}_3$ , and the defects responsible for the 565-nm band<sup>27</sup> and the spin-one ESR spectrum<sup>32</sup> in  $\text{NaN}_3$ . The latter defects remain unidentified, as does the defect responsible for the 565-nm band in  $\text{KN}_3$ .<sup>30</sup> The most plausible model for all of these defects is a self-trapped electron

(substitutional  $N_3^{2-}$ ), but conclusive evidence is lacking. The  $N_3^{2-}$  ESR spectrum has been observed in  $Ba(N_3)_2$ <sup>49</sup> and  $KN_3$ ,<sup>25</sup> but has not been correlated with any optical absorption. The ESR spectrum of isolated  $N_3^{2-}$  has not been seen in  $NaN_3$ , but the spin-one spectrum may be due to exchange-coupled pairs of self-trapped electrons, perhaps associated with anion vacancies. It also remains to discover independent evidence for cyclic  $N_3$ <sup>50,51</sup> which has been proposed in order to explain far-infrared spectra,<sup>4</sup> and to calculate its properties.

Ab-initio molecular orbital calculations on low-lying states of  $N_3^-$ <sup>42</sup> support the interpretation of fundamental optical absorption spectra of alkali azides as internal transitions of the azide ion,<sup>40</sup> and explain their fluorescence spectra as transitions between bent excited states of  $N_3^-$ .<sup>41</sup> In addition, these calculations may help elucidate the mechanism of photolysis in alkali azides. The long radiative lifetime and relatively small relaxation energy of the  $^1A_2(^1\Sigma_u^-)$  state are compatible with efficient energy transfer between azide ions;<sup>52</sup> thus mobile excitons, which have been invoked by many investigators,<sup>24</sup> are clearly feasible. The  $^1\Sigma_u^-$  state ultimately decays by intersystem crossing to  $^3A_2(^3\Sigma_u^-)$ , followed by a radiative transition to metastable  $^3B_2(^3\Sigma_u^+)$ . This metastable state of  $N_3^-$  may play a role in photolysis, in that it may be the precursor of the decomposition reaction:  $N_3^{*-} + N_3^- \rightarrow 3N_2 + 2e^-$ . (A variety of alternative reaction products is possible, including F and  $F_2^+$  centers, substitutional and interstitial  $N_2^-$ , substitutional  $N_4^-$  and  $N_3^{2-}$ , etc.)

The mechanism of defect production is the fundamental problem in alkali azides. Now that a number of defects have been identified and characterized, the most fruitful approach to the solution of this problem

would involve detailed studies of the kinetics of defect production. Thus far only preliminary measurements have been made, with somewhat contradictory conclusions.<sup>24,30</sup> The independent parameters to be varied are temperature and radiation dose and intensity, and excitation wavelength, while the spectra to be monitored include optical absorption, fluorescence, and ESR. Irradiation in the temperature range between 4.2 K and 77 K, where the  ${}^3B_2({}^3\Sigma_u^+)$  state of  $N_3^-$  may be stable and detectable by ESR, should be particularly fruitful. A considerable gain in information and reliability could be achieved by monitoring spectra during irradiation. A synchrotron light source would greatly facilitate measurement of the various excitation spectra.

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